

10 Japanese Patent Office (JP)
11 Public Patent Application
12 Public Patent Announcement
1993-320358
43 Published Dec. 3, 1993

51 Int. Cl. 5
C 08 H 1/06
B 44 C 5/06

Identification Code NVD
Internal Reference Number 8215-4J
F 9134-3K

Request for substantive examination, not requested Number of Claims: 4 (6 pages total)

54 Name of Invention Production Method For Water-soluble Keratin

21 Patent Request No. 1992-174659
22 Application Date May 22, 1992

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(54) [Invention Name] Keratin Protein High Pressure Molded Article

(57) [Abstract]

[Composition] A keratin protein high-pressure molded article that is obtained through high pressure molding of compounds that consist only of keratin fine powder or fiber, or consist of keratin fine powder or fiber and a binder or other additive that makes up less than 50% of the sum total weight.

[Effect] A new raw material that can substitute for natural raw materials like ivory, tortoise shell, and seal stock, made from the natural keratin powder or fiber fragments from the feathers, hair, horns and hoofs of birds and animals.

[Scope of this patent application]

[Claim 1] A keratin protein high-pressure molded article that is obtained through high pressure molding of compounds that consist of keratin fine powder or fiber and a binder or other additive that is added in a desired amount that makes up less than 50% of the sum total weight.

[Claim 2] The keratin from the hooves, horns, beaks, nails, scales, shells, fur, feathers, wool and hair cuttings of birds and other animals in the form of a powder or fiber that has an average size of at least $0.1\mu\text{m}$, is a molded article mentioned in Claim 1

[Claim 3] The binder made from natural materials selected from the likes of partially degraded protein, gelatin, glue, collagen, casein, milk, egg whites, starch, cystine, cysteine, thioglycolate, fats, rhodine, sap or natural rubber (NR) and/or synthetic resins selected from the likes of epoxy resin, melamin resin, urea resin, polyester resin, polychlorinated biphenyl resin, poly-amino acid resin, PVA, polyolefin resin, and synthetic rubbers like SBR rubber, IR rubber, or BR rubber, is a molded article mentioned in Claim 1.

[Claim 4] The above-mentioned additive agents are cross-linking agents, are molded articles mentioned in Claim 1.

[0001]

[Invention Specification]

[Technical Field] This invention is high pressure molded articles, as well as things related to the denatured particles obtained from the pulverization of them, such as artificial ivory, tortoise shell, piano keys, seal stock, makeup compacts, ornaments, tires, or seats, obtained from a high pressure molding that consists of keratin powder or fibers, or a composite including it as the main ingredient.

[0002]

[Conventional Art] Traditionally, while things like tortoise shell, water buffalo horn, or ivory have been important as raw materials for items such as personal seals, piano keys, and ornaments, because international animal protection has changed the background of society, and the importation and use of these natural raw materials has become difficult, there is a demand to develop a substitute raw material, as well as particles used in spike tires to develop things like studless tire treads that can be used to resolve pollution.

[0003] This kind of substitute raw material can be developed into, for example, a molded article of methyl methacrylate resin or unsaturated polyester resin with magnesium hydroxide, aluminum hydroxide, titanium oxide, or calcium carbonate added as an inorganic filler material; or artificial ivory from eggshell hardened with milk casein. However, these raw materials are made to retain both hydrophilic and hydrophobic qualities, and it is impossible to avoid the demand to make satisfying qualities such as solidity, carvability, and tactile nature.

[0004] Recently, silk thread, wool, and chicken feathers have been pulverized into a powder and dissolved with an organic solvent, and the hard proteins like keratin and collagen, removed as a thin film, overlapping a number of these to see if an substitute product for tortoise shell can be obtained, however, since research has only just started, sufficient results have not yet been obtained.

[0005]

[The Problem This Invention Proposes To Resolve] Therefore, this purpose of this invention is to achieve molded article raw materials having every kind of physical

property, tactile sense, carving manufacturability in which the conventional substitute raw materials have not made achievements, and things such as artificial ivory, personal seals, piano keys and tortoise shell ornaments that can be obtained through manufacture.

[0006]

[Procedures For Resolving The Problem] The invention purpose stated above will be achieved by the invention by means of a keratin protein high-pressure molded article that is obtained through high pressure molding of compounds that consist of keratin fine powder or fiber and a binder or other additive that is added in a desired amount that makes up less than 50% of the sum total weight.

[0007] This invention consists of keratin powder or fibers, or a compound of these where they are the main ingredient, directly made into molded articles by a high pressure mold, the primary characteristic of the keratin raw material is that it can be used as is.

[0008] The keratin used in this invention is the powder or fibers of the hooves, horns, beaks, nails, scales, shells, fur, feathers, wool and hair of various birds and animals, of an average size greater than 0.1 μm , on the order of several mm. When speaking here about the average size, there is a difference between the average diameter of the powder and the larger average diameter of the fibers. This powder or fiber can be used as described above as a natural raw material without modification, or it may be obtained after prior processing to pulverize it, or freeze and pulverize it. (Application 1991-25661).

[0009] The keratin powder or fibers can be used alone, or a mixture of 2 or more can be used, in the high pressure mold, they must be at least 50% and as much as 100% of the total compound's total weight, and preferably have a ratio of 70-95% by weight. Since strength is difficult to achieve at greater than 95%, a useful goal should be up to 95% by weight. On the other hand, when the ratio falls below 50% by weight, there is a tendency to lose the natural texture.

[0010] Binders such as partially degraded protein, gelatin, glue, collagen, casein, milk, egg whites, starch, cystine, cysteine, thioglycolate, fats, rhodine, sap or natural rubber (NR) and/or synthetic resins selected from the likes of epoxy resin, melamin resin, urea resin, polyester resin, polychlorinated biphenyl resin, poly-amino acid resin, PVA, polyolefin resin, and synthetic rubbers like SBR, IR, BR, CR, EPM, EPDM, can be added as desired, used alone, or in a mixture of 2 or more.

[0011] Components other than those listed above can optionally be made ingredients, other publicly known additives such as resins, filling agents, dyes, colorants, reinforcement agents, cross-bridging agents, and solvents can be mixed. However, binders and other additives should not exceed 50% of the total weight of the mixture, if this is not done, one cannot hope but to lose the compound's natural feeling.

[0012] In a particularly nice concrete example, a small amount of cross-bridging agent, coupling agent is mixed. This cross-bridging agent can be, for example, a 2,4-toulene diisocyanate prepolymer adduct, epoxy resin, or a chemical compound like, a silane coupling agent, an organic metal coupling agent, melamine, formalin, benzoguanamine, urea, thioglycolate, cysteine, or fats with double bonds, and when used during the molding, a cross bridging reaction takes place by reacting with a reaction functional group such as hydroxyl, carboxyl, or an amino group on the surface of the keratin, obtaining a molded article with an excellent solidity characteristic.

[0013] In this invention, the compound described above directly becomes a molded article by high pressure molding. When this happens, the twisting of the keratin particle

space or fiber space causes repolymerization, at the same time that this is occurring, because there is a cross-bridging agent, the keratin molecules cross-bridge with similar molecules freely. With respect to high pressure molding, examples of methods for super high pressure molding used by solid super high pressure presses include warm isothermal pressing (WIP method), and cold isothermal pressing (CIP method); or if injection molding, compression molding or high pressure molding methods are carried out by high pressure molding, the highest pressure for warm isothermal pressing is 10,000 kg/cm² at a temperature of 20-200° C, and 6,000 kg/cm² at room temperature for cold isothermal pressing, so the 10 ton / cm² of the solid super high pressure press is preferred.

[0014] Also in regards to molding, the composite can be made using a uniform compound as normal, however, stratification, like those seen in the rings of a tree can occur in spite of the desired result.

[0015] It is possible to obtain useful molded goods by mold manufacturing artificial ivory, personal seals, piano keys, tortoise shell ornaments, makeup compacts, printing materials and tires that possess excellent outward appearance, feel, water absorptiveness, oil absorptiveness, and carvability, using this invention's methods.

[0016] This invention is explained in the following example of execution.

[Example of Execution 1] Personal Seal Materials (Artificial Water Buffalo Horn)

Compound	W/W%
1) Pulverized bovine hoof powder	70.0
2) Bovine bone powder	10.0
3) Epoxy Resin (Epikote1004)	20.0 (powder softening point 97° C)
Total	100.0

[0017] 20g of the epoxy resin powder and 10g of the bovine bone powder were prepared in the "Raikai" device and ground for one hour. 70g of the pulverized bovine hoof powder were added to this mixture, and it was mixed uniformly. A cylindrical metal pattern, 18mm in diameter, and 150mm in length, placed in a degassing device, was filled with this entire compound, and while degassing, pressure is applied from above and below, and heat was increased until they reached 200 kg/cm² and 130° C and were maintained for 2 hours. The molded article was removed from the metal pattern and evaluated for appropriateness as a personal seal.

[0018]

Chart 1

	Example of Execution 1	Comparison Test 1 (Store bought – made of water buffalo horn)	Comparison Test 2 (Store bought – made of phenol resin)
Outward Appearance	B	A	C
Feel	A	A	C
Carvability	B	B	C
Red Ink Adhesion	A	A	B
Red Ink Marking	A	A	B

Water-based Ink Adhesion	B	B	D
Water-based Ink Marking	B	B	D
Solidness	A	A	A
Durability	B	B	B

It was confirmed that if the outward appearance was adjusted, it had the capacity to be a suitable replacement for the natural water buffalo horn materials.

[0019]

[Example of Execution 2] Artificial Tortoise Shell

Compound	W/W%
1) Pulverized bird bones and chicken feathers (white)	85.0
2) Pulverized bird bones and chicken feathers (black)	5.0
3) Hexamethylene Diisocyanate (HMDI) Prepolymer	10.0
Total	100.0

[0020] 10g of HMDI prepolymer was dissolved in 100g of acetone, and to this was thrown in the 2 types of pulverized bird bones and chicken feathers, this mixture was uniformly distributed. The acetone was quickly removed in a vacuum at room temperature, and the feather powder surface was processed in the HMDI prepolymer. A stencil with a 100mm internal diameter, and a height of 50mm was filled with this processed feather powder, which was compression molded in a super high pressure press, gradually raising the temperature and pressure to 100° C and 100 ton / cm², and maintained for one hour. The molded article obtained had a semi-transparent luster. This was compared with a naturally harvested tortoise shell.

[0021]

Chart 2

Results	Example of Execution 2	Comparison Test 1 Natural Tortoise Shell
Outward Appearance	A	A
Feel	A	A
Processability	A	A
Solidness	A	B
Durability	A	B

[0022] The ration of black and white pulverized feather powder is graded, because of artificial looking false streaks arising in the manufacture, or, alternatively, it is possible to have different look using a laminate mold.

[0023]

[Example of Execution 3] Tire Treads [Keratin Tire]

Compound	W/W%	Surface processing
1) Pig hair (fragments)	40.0	"
2) Bovine hoof powder	20.0	"

3) Silane Coupling Agent	2.0	"
Total	62.0	
4) NR (Natural Rubber)	36.5	
5) Sulfur	1.0	
6) Vulcanizing accelerator (DPG)	0.3	
7) Vulcanizing accelerator (MBT)	0.2	
Total	100.0	

DPG (diphenylguanidine); MBT (2-mercaptobenzothiazole)

[0024] Keratins (1) and (2) were surface processed with the silane coupling agent (3), which had been diluted with ethyl acetate, and then were dried. These surface processed ingredients were added to components (4) through (7) and combined together in a kneader. These combined ingredients were vulcanization molded into tire treads using the WIP method (warm isostatic pressing) at 135° C and 8,000 kg / cm² for 30 minutes.

[0025] The molded article obtained was cut into 3cm x 5cm flat strips with no pattern and its physical characteristics were evaluated. For the comparison with a normal rubber tire, a 165SR13 radial tire tread commercial product was used, and for the studless rubber tire, a 165R13 studless tire tread was used, and both were cut into similar strips for the conduction of the comparison tests.

[0026]

Chart 3

No.	Type	Slip Resistance Index	Abrasion Resistance Index
1	Example of Execution (Keratin Tire Tread group)	190	80
2	Comparison Example (Commercial Product 165SR13 Radial Tire Tread Group)	100	100
3	Comparison Example (Commercial Product 165R13 Studless Tire Tread Group)	140	70

[0027] Testing Methods

Slip Resistance Index

The test was carried out using a constant velocity style, rotating disk type abrasion testing device. Ice with a smooth surface was affixed to the approximately 20cm in diameter rotor plate, and the 3cm x 5cm test strips were pushed down by a fixed weight (500g). When the rotating disk was spinning at a constant speed, the friction force placed on the test strip was measured with a load cell. The comparison test material's friction force was measured and set at 100 (the index value), the higher the score, the greater the friction force, and therefore the better the slip resistance.

Abrasion Resistance Index

Using the testing method described above, asphalt was placed on the surface of the rotating disk, and in the same manner, the rotor was operated for a fixed amount of time, and the ratio of remains (the abrasion resistance ratio) was taken, the abrasion resistance

of the comparison test material was set at 100 (the index value). The higher the score, the better the abrasion resistance.

[0029] The keratin tires made from this example of execution make good all weather tires, that have anti-slipping qualities on all road surfaces, including rainy roads, snowy and icy roads, or oily roads, as well as being completely non-polluting. Also, when it is time to discard them, and they are returned to the earth, they become a good organic fertilizer, and cause almost no harm to the environment.